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# Uptake of Tridodecylmethylammonium Chloride by PVC

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## Synopsis

The uptake of tridodecylmethylammonium chloride (TDMAC) by poly(vinyl chloride) has been investigated to provide a more quantitative basis for the preparation of blood-compatible surfaces based on TDMAC–heparin coatings. Sorption isotherms of TDMAC from toluene–cyclohexane and toluene–methanol mixtures have been measured. In toluene–cyclohexane mixtures, the TDMAC uptake is proportional to the degree of swelling of the polymer. From ion-exchange experiments with $^{36}Cl^-$, it appears that only a small fraction of the TDMAC remains near the PVC surface to provide the heparin binding capacity. Methanol forms a strong H-bonded complex with TDMAC in toluene and prevents its sorption by PVC.

## INTRODUCTION

The quaternary ammonium salt tridodecylmethylammonium chloride (TDMAC) has been extensively used in biomedical materials technology for the preparation of nonthrombogenic surfaces. The compound can be applied to polymeric materials by adsorption from organic solvents, resulting in a small ion exchange capacity on the surface of the material, which can be used to bind ionically the anticoagulant polyelectrolyte heparin.[1] Materials which are "heparinized" in this way have very favorable properties with respect to the absence of initiation of blood coagulation, and their application in a variety of therapeutic and diagnostic fields is currently under investigation.[2,3] A quantitative description of the attachment of TDMAC to polymers has been lacking up to now.

Within the scope of our research in the field of blood-compatible surface coatings, we report here on the solution and adsorption behavior of TDMAC. As a polymeric adsorbent, poly(vinyl chloride) was chosen. Several solvent systems have been investigated to relate the TDMAC uptake to polymer swelling and to solution behavior.

## EXPERIMENTAL

### Materials

TDMAC was obtained from Polysciences Inc. Poly(vinyl chloride) powder was Breon S 110/10, a very pure preparation according to elementary analysis

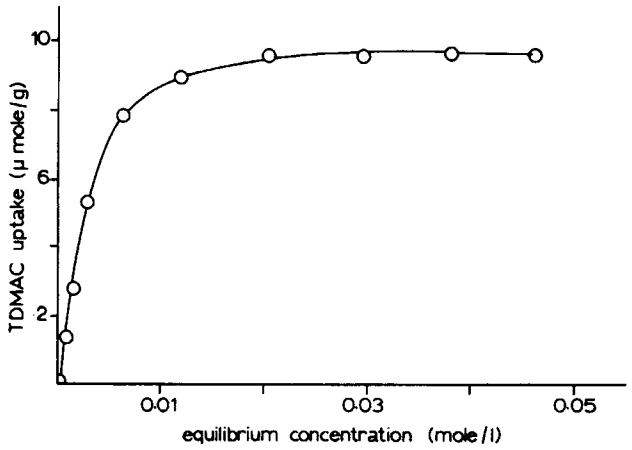


Fig. 1. Sorption isotherm of TDMAC by PVC from toluene solution at 20°C.

and IR spectrum. From gel permeation chromatography (solvent, tetrahydrofuran; stationary phase, Styragel, Waters Associates), the molecular weight distribution was calculated[4,5] as $\bar{M}_n$ = 28,000, $\bar{M}_w$ = 56,000, using calibration samples of PVC from Pressure Chemical Co. The surface area of the PVC powder was determined as 1.0 $m^2/g$ by the BET method with nitrogen adsorption, using a Perkin-Elmer Model 212D Sorptometer.

## Methods

Adsorption experiments at which 5 g PVC was equilibrated with 25 ml of the appropriate solutions were carried out at 20° ± 0.5°C. TDMAC-loaded PVC powders were separated from toluene solutions by filtration, followed by repeated rapid washings with small quantities of toluene, and dried *in vacuo* at 45°C for 48 hr. TDMAC concentrations were determined by the titration method described by Cross[6] and Patel.[7] Swelling experiments were carried out as described before.[8] Radiotracer experiments to determine ion exchange capacity of TDMAC adsorbates were performed at the Interuniversitary Reactor Institute, Delft, The Netherlands, using an aqueous $^{36}Cl^-$ solution ($Na^{36}Cl$, The Radio-

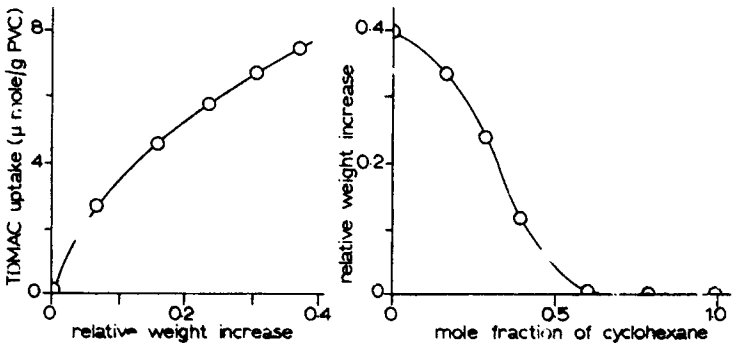


Fig. 2. Swelling of PVC and TDMAC sorption in 5.25 × $10^{-3}M$ solution in toluene–cyclohexane mixtures at 20°C.

TABLE I
Chloride Exchange of TDMAC Adsorbates with $^{36}Cl^-$

| Total TDMAC present, μmole/g PVC | Exchangeable $Cl^-$, μmole/g PVC |
|---|---|
| 4.247 | 0.0515 |
| 6.056 | 0.2167 |
| 7.125 | 0.3051 |

chemical Centre) with a specific activity of 0.340 Ci/mole. Radioactivity measurements were carried out on a Packard TriCarb Model 3320 liquid scintillation counter, using the Packard "Instagel" scintillation medium. Gas-chromatographic separations of toluene–methanol mixtures were performed at 152°C on Porapak Q columns. Light-scattering measurements were performed at 25°C on a Fica-50 photogoniodiffusiometer with unpolarized light of 546 mm. IR spectra were recorded on a Beckmann IR-33 spectrometer equipped with Beckmann liquid cells with NaCl windows and Teflon spacers, optical path 1.2 mm.

## RESULTS AND DISCUSSION

The adsorption isotherm of TDMAC on PVC from toluene solution is given in Figure 1. The plateau value of adsorption, 10.27 μmole/g, combined with the BET area of 1.0 $m^2/g$, corresponds to an improbably small area of 16 $Å^2$/molecule, assuming monolayer adsorption on the polymer surface. It can be concluded that the TDMAC is not only present on the PVC surface, but does actually dissolve into the toluene-swollen polymer. This is confirmed by the relation between degree of swelling and TDMAC uptake of PVC in toluene–cyclohexane mixtures (Fig. 2).

The fraction of TDMAC remaining near the polymer surface, thus contributing to the ion-exchange capacity, was determined by $^{36}Cl^-$ exchange of TDMAC-loaded PVC. Let there be $x$ exchangeable $Cl^-$ ions on the PVC surface and $m$ $^{36}Cl^-$ ions in solution before equilibration. After equilibration, there remain $n$ $^{36}Cl^-$ ions in solution. At equilibrium, the $^{36}Cl^-/Cl^-$ ratio on PVC and in solution should be equal:

$$\frac{x - m + n}{m - n} = \frac{m - n}{n} \tag{1}$$

TABLE II
Light Scattering of TDMAC in Toluene/Methanol[a]

| Methanol concentration, mole/l. | TDMAC concentration, mole/l. | Dissymmetry factor |
|---|---|---|
| 0 | 0.0525 | 1.706 |
| 1.312 | 0.0525 | 1.204 |
| 0 | 0.00525 | 1.081 |
| 0.1312 | 0.00525 | 1.035 |

[a] $\lambda$ = 546 mm (unpolarized).

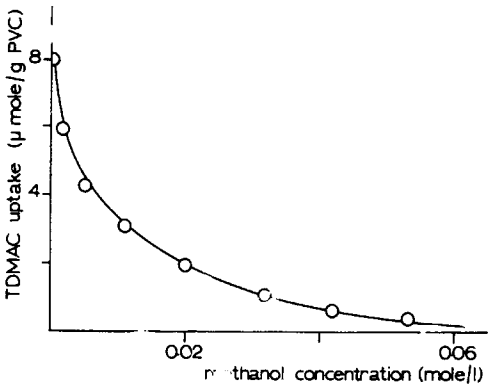


Fig. 3. TDMAC sorption by PVC from $5.25 \times 10^{-3}M$ solution in toluene–methanol mixtures at 20°C.

from which follows that

$$x = (m/n)\,(m - n) \tag{2}$$

The results with three different TDMAC loads are given in Table I. It is obvious that only a small fraction of the TDMAC is present on the PVC surface.

The TDMAC uptake in toluene–methanol mixtures is given in Figure 3. Nothwithstanding the enhanced swelling caused by added methanol,[8] the TDMAC uptake is greatly reduced by small amounts of methanol and approaches already a zero level at methanol concentrations at which swelling is hardly influenced. This is not caused by selective adsorption of methanol which might prevent the TDMAC uptake, as was shown by gas chromatography of toluene–methanol mixtures before and after treatment with PVC. The swelling behavior is not influenced by TDMAC.

It is well known that trialkylammonium salts with eight or more C atoms per carbon chain do not form well-defined "inverted micelles" in toluene or cyclohexane solution, contrary to smaller oil-soluble surfactant molecules, but rather tend to form stepwise aggregates depending on surfactant concentration.[9,10] Light-scattering data of TDMAC in toluene with added methanol are given in Table II. From the dissymmetry factor, i.e., the ratio of light-scattering intensities at angles of 45° and 135°, the size of particles of known shape may be determined.[11] From the decrease of the dissymmetry factor when methanol is added, it can be concluded that the TDMAC aggregates in toluene are largely broken up by methanol. The formation of a strong hydrogen-bonded complex between methanol and TDMAC was demonstrated by IR spectroscopy[12] of $0.1M$ $CD_3OD$ in toluene, which showed a wavelength shift of the O—D adsorption from 2680 $cm^{-1}$ to 2510 $cm^{-1}$ when TDMAC was added to a concentration of $4.3 \times 10^{-3}M$. It is probable that the formation of the methanol–TDMAC complex makes the interaction between PVC and TDMAC thermodynamically unfavorable, thus diminishing the TDMAC uptake.

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